Indian J. Phys. **79(2)**, 153-156 (2005)

AN INTERNATIONAL JOURNAL
IJP

Ultrasonic analysis in the ternary mixtures of 1,4 dioxane + carbon tetrachloride + 1-butanol

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Received 1 November 2004; accepted 20 December 2004

Abstract : The values of sound velocity, density and viscosity have been measured at 308 K in the system 1,4 dioxane + carbon tetrachloride + 1-butanol. From these data, acoustical parameters such as adiabatic compressibility, free length, free volume and internal pressure have been estimated using the standard relations. The results are interpreted in terms of molecular interaction between the component of the mixtures. 1-Butanol is found to be a good structure maker, that makes the carbon tetrachloride-1,4 dioxane complexes. The presence of weak interactions are confirmed in the ternary system.

Keywords : Ultrasonic velocity, acoustic parameter, dipolar and dispersive interactions.

PACS No. : 43.35 Bf

1. Introduction

In many industrial applications, liquid mixtures rather than single component liquid system are used in processing and product formulations. Thermodynamic and transport properties of liquid mixtures have been extensively used [1,2] to study the departure of a real liquid mixture from ideality. A departure from linearity in the velocity *versus* composition behaviour in liquid mixtures is taken as an indication of the existence of interaction between the different species [3,4]. During the last few decades, ultrasonic study of liquid mixtures has gained much importance in assessing the nature of molecular interactions and investigating the physico-chemical behaviour of such system [5,6]. Though, a number of investigations were carried out in liquid mixtures having alcohol as one of the component, ternary system with 1-butanol as one of the component are scarcely reported.

Further, as alcohols are highly polar, they can be made to form azeotropes with one or other component of the binary complexes. The binary complexes taken up for the present study is 1,4 dioxane + carbon tetrachloride, both are symmetric and hence non-polar. It will be interesting to study the influence of an asymmetric molecule in a symmetric molecular environment. Though the alcohol molecule is in a symmetric molecular environment, the environment is not fully symmetric. This asymmetric environment by symmetric molecules is expected to interact differently with a polar molecule such as alcohol. Hence, the authors have performed a thorough study on the molecular interaction studies of 1,4 dioxane + carbon tetrachloride + 1-butanol, using the sound velocity data. The present work deals with the measurements of ultrasonic velocity and computation of related parameters in the ternary system of 1,4 dioxane + carbon tetrachloride + 1-butanol at 308 K.

2. Experiment

The mixtures of various concentration in mole fraction were prepared by taking purified AR grade samples at 308 K. The mole fraction of the second component, carbon tetrachloride (x_2 = 0.3) was kept fixed, while the mole fraction of the remaining two were varied from 0.0 to 0.7, so as to have the mixtures of different compositions.

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The ultrasonic velocities in liquid mixtures have been measured using an ultrasonic interferometer (Mittal type) working at 2 MHz frequency with an ccuracy of ±0.01 ms^{-1}. The density and viscosity are measured using a pycknometer and an Ostwald's viscometer, respectively with an accuracy of 3 parts in 10^5 for density and 0.001 Nsm^{-2} for viscosity.

Using the measured data, the acoustical parameters such as adiabatic compressibility (β), free length (L_f), free volume (V_f) and internal pressure (π_i) and their excess parameters have been calculated using the following standard expressions :

$$\beta = \left(U^2 \rho\right)^{-1}, \tag{1}$$

$$L_f = K_T \beta^{1/2}, \tag{2}$$

$$V_f = \left[\frac{M_{eff} U}{\eta k}\right]^{3/2}, \tag{3}$$

$$\pi_i = bRT\left[\frac{k\eta}{U}\right]^{1/2}\left[\frac{\rho^{2/3}}{M_{eff}^{7/6}}\right], \tag{4}$$

$$A^E = A_{exp} - A_{id}, \tag{5}$$

and

$$A_{id} = \sum x_i A_i, \tag{6}$$

where the notations have the usual meaning.

3. Results and discussion

The experimental values of density, viscosity and velocity at 308 K for the pure components and for the system 1,4 dioxane + carbon tetrachloride + 1-butanol are given in Table 1.

Table 1. Values of density (ρ), viscosity (η) and velocity (U) at 308 K.

Mole fraction		ρ	$\eta \times 10^3$	U
x_1	x_3	kg m^{-3}	Ns m^{-2}	ms^{-1}
1.0000	0.0000	1032.0	1.4220	1310.2
0.0000	0.0000	1574.8	0.7855	953.4
0.0000	1.0000	810.0	1.3990	1217.8
0.0000	0.7000	923.1	1.3972	1167.4
0.0999	0.5999	950.0	1.3234	1178.0
0.2000	0.4999	979.0	1.1409	1190.3
0.2999	0.3999	1006.5	1.0111	1201.2
0.4000	0.2998	1034.0	0.9699	1212.2
0.4999	0.1999	1062.2	0.9561	1221.4
0.6000	0.0999	1090.9	0.9513	1230.1
0.7000	0.0000	1118.6	0.9439	1242.2

The calculated values of adiabatic compressibility (β), free length (L_f), free volume (V_f) and internal pressure (π_i) at 308 K for the pure components and for the mixtures are presented in Table 2. The respective excess values at the said temperature have been calculated and are shown in Figures 1 to 4.

Table 2. Values of adiabatic compressibility (β), free length (L_f), free volume (V_f) and internal pressure (π_i) at 308 K.

Mole fraction		$\beta \times 10^{10}$	$L_f \times 10^{10}$	$V_f \times 10^7$	$\pi_i \times 10$
x_1	x_3	Pa^{-1}	m	$m^3 mol^{-1}$	Pa
1.0000	0.0000	5.6447	0.4778	8.2609	191.71
0.0000	0.0000	6.9851	0.5315	6.2986	377.06
0.0000	1.0000	8.3241	0.5802	5.8531	205.33
0.0000	0.7000	7.9484	0.5670	4.9039	250.13
0.0999	0.5999	7.5848	0.5539	5.5574	241.36
0.2000	0.4999	7.5088	0.5399	7.2641	222.21
0.2999	0.3999	6.8852	0.5277	9.0866	207.41
0.4000	0.2998	6.5812	0.5159	10.0880	201.37
0.4999	0.1999	6.3104	0.5052	10.7206	198.41
0.6000	0.0999	6.0575	0.4950	11.2239	196.48
0.7000	0.0000	5.7935	0.4840	11.8399	193.91

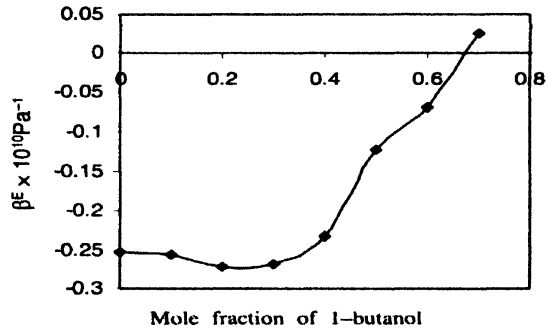

Figure 1. Mole fraction *vs.* excess adiabatic compressibility at 308 K

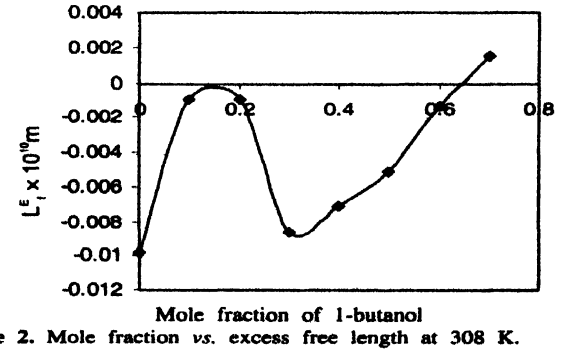

Figure 2. Mole fraction *vs.* excess free length at 308 K.

It is found that the ultrasonic velocity decreases with increasing concentration of 1-butanol. An exactly reverse trend, as expected, is noticed in the variations of adiabatic compressibility. The ease with which a medium can be

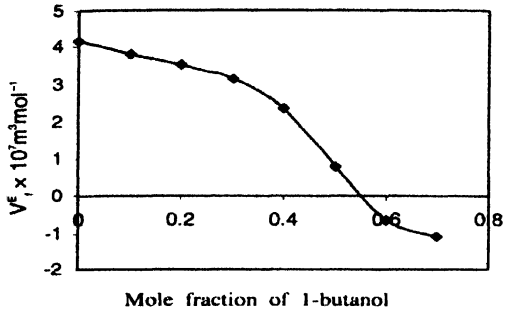

Figure 3. Mole fraction *vs.* excess free volume at 308 K.

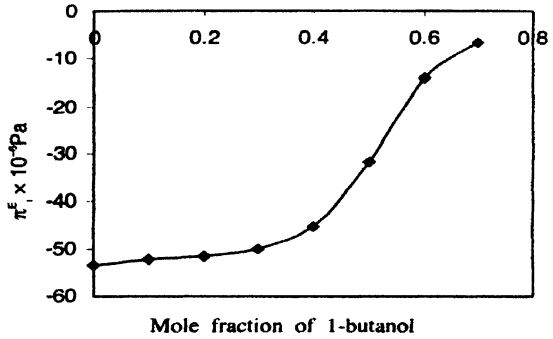

Figure 4. Mole fraction *vs.* excess internal pressure at 308 K.

compressed is given by the compressibility values. The higher compressibility value reveals that the medium is loosely packed. Table 2 shows that as alcohol concentration is increased, the compressibility values also increase. Thus, the addition of alcohol molecules disturbs the available symmetry in the einvironment and ruptures the bonds in between the species. Hence, the components of the mixtures are set far away and it makes the sound velocity to decrease. As the number of hydrocarbon group decreases, the sound velocity is found to decrease, as is evident from Table 1. This behaviour at such concentrations for the mixtures, which is different from the ideal mixture behaviour, can be attributed to the intermolecular interactions in the system studied [7–10].

Among the three components, both 1,4 dioxane and carbon tetrachloride are symmetric and non-polar. The electronegativity of oxygen (3.5) is higher than all other atoms of the environment in the entire concentration range of the mixtures. However, in the absence of alcohol molecules, the oxygen of 1,4 dioxane is not supposed to interact appreciably with chlorine atoms of carbon tetrachloride as the electronegativity of chlorine is 3.0. Further, the perfect symmetry arrangement of carbon tetrachloride prevents the attraction of electron by oxygen of 1,4 dioxane and so there would be almost no interaction between these two components. But the situation is reversed if the third component, 1-butanol is added.

In the case of 1,4 dioxane, neither oxygen nor carbon is equally influenced by its neighbouring atoms as carbon in carbon tetrachloride. Hence, when the third component is added, it disturbs the 1,4 dioxance molecule rather than carbon tetrachloride. Thus, the compactness of the medium is lost and the medium seems to be more and more rarefied with increasing alcohol concentration. As the 1-butanol concentration decreases, the number of interacting molecules which can break the molecular clustering of the other is reduced and hence, the dipole formation is restricted. This suggested that the interaction existing between the 1-butanol and 1,4 dioxane is strengthened and there will be an increase in cohesive energy. So, the free length increases in the mixture with increasing 1-butanol concentration.

On the basis of sound propagation in liquid [11], the increase in free length after mixing, decreases the sound velocity. This is also in accordance with the expected decrease in compressibility following an increase in ultrasonic velocity with decreasing 1-butanol concentrations in the mixture. The intermolecular free length is found to be a predominant factor in determining the nature of sound velocity variation in liquid mixtures [12]. In this system, the adiabatic compressibility is increasing with rise of 1-butanol concentration, showing thereby a progressively strengthening of intermolecular interaction. Similar results in some liquid mixtures were reported by Bhatti and Singh [13] and Palaniappan *et al* [14].

From Table 2, it is noticed that as the concentration of 1-butanol decreases, free volume increases whereas the internal pressure decreases. This suggests the loose packing of molecules inside the shield, which may be brought about by the decreasing magnitude of interactions [14,15].

In order to substantiate the presence of interaction between the molecules, it is essential to study the excess parameters. The deviation of a physical property of the liquid mixtures from the ideal behaviour, is a measure of the interaction between the molecules which is attributed to either adhesive (or) cohesive forces [16].

The excess adiabatic compressibility (Figure 1) and the excess free length (Figure 2) are mostly negative and indicate the presence of an AB interaction (here alcohol-dioxane). A large steep increase in β^E at 3% of alcohol reflects the strong AB or AC interaction leading to complexation. The relative magnitudes of β^E show that the strength of AB interaction decreases as the alcohol concentration increases. The small values of β^E in the

lower mole fractions of alchohol, shows that the AB and AC interactions are of nearly the same strength as BC. On the other hand, at higher mole fraction, the large deviation of β^E reflects the strengthening of AB interactions than the others.

The role of AB interaction with regards to effective molecular size appears to differ from liquid to liquid [17]. The nature of AB interaction existing in the present system is such that it increases the effective molecular size and thus, leads to negative L_f^E values. An interaction between the hydroxyl group of the alcohol and the ethane/ oxide group of 1,4 dioxane produces a large strain in the ring. This produces opposite pole at the other end of the ring. This increased dipolar character of the 1,4 dioxane is responsible for the observed larger strength of AB interactions. These effects are well pronounced at higher mole fraction of alcohol and hence, L_f^E becomes positive at 0.7 mole fraction of 1-butanol.

The presence of electron donor group, Cl^- in carbon tetrachloride and OH^- in alcohol, increases the electron density in the medium and hence, the AB interactions overrule the possibility of other interactions. The observed AC interactions is due to the presence of OH^- of alcohol and Cl^- of carbon tetrachloride, whereas the BC interactions are due to the existence of negative polarity in both molecules. The AB interactions in the mixtures therefore, may be of the dipole-induced dipole type. The carbon tetrachloride molecule may therefore, be distorted in polarisation process [18] which clearly explains the observed negative V_f^E values at higher mole fractions of alcohol. However, at lower mole fractions, as the role of alcohol molecules are highly restricted, the available space between the components is undisturbed and hence V_f^E shows positive values. It is interesting to note that the variation in the internal pressure values and their deviations behave exactly in a reverse trend as that of free volume. Such a behaviour is also observed by Devinder Pal and Bhatti [19] in some ternary liquid mixtures. The negative excess internal pressure in the mixtures clearly confirms this view.

4. Conclusion

The derived acoustical parameters and their positive excess values hint to the presence of weak dipolar and dispersive interactions between the component molecules in the mixtures studied and the inherent nature of alcohols predominate the existing dispersive interactions.

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